Section 10

HEALTH AND SAFETY ISSUES

Quick Reference Data

Toxicity

Toxic Dosage
(for 70 kg adult human)

	mls
Gasoline	115-470
Diesel Fuel	63
Methanol	60-240
Ethanol	

Dispersal in Water-Borne Spills

Gasoline	slow - by evaporation and water action
Diesel fuel	slow - by evaporation and water action
Methanol	rapid - 100% soluble in water
Ethanol	rapid - 100% soluble in water

Useful Terms and Definitions (also see Glossary)

- **Butanethiol:** a substance with a strong, offensive and unique odor, used as a fuel malodorant to provoke instant recognition by the public as methanol.
- **Nigrosine:** a dye, to be added in small amount (up to 15% volume) to methanol to enhance the luminosity of methanol flame.
- **Toxicity:** the quality, state, or relative degree of being poisonous.

Key Issues and Implications

Issue #1: Toxicity

Methanol is highly toxic if ingested, and, in relatively small quantities can cause blindness or death. Poisoning can also occur by inhalation of methanol vapors or by prolonged skin exposure. There is a high potential for unintentional ingestion of methanol since it is odorless, colorless, and tasteless. In contrast, the toxicity of ethanol is quite low, being only toxic if ingested in very large quantities.

Implications of Toxicity:

- Special handling procedures will be needed for all phases of methanol production, shipping, blending, and retail sales to prevent inadvertent poisoning or unnecessary exposure.

Proposed Solutions:

- Additives need to be developed for neat methanol fuels that will provide a distinct/unique odor and unpleasant taste to methanol, as well as a distinguishable flame color for safety.
- Mechanical systems will have to be installed on methanol fuel tanks and refueling points to prevent syphoning or accidental ingestion.

Detailed Information: Refer to page 10-1 through 10-5.

Issue #2: Water Contamination

Alcohol leaks and spills on surface and subsurface water can harm animal and plant ecosystems.

Implications of Water Contamination:

- Ethanol disperses quickly and is highly biodegradable in the environment; ethanol is also less toxic to marine life and less costly to clean up than petroleum-based fuel spills. As a result, ethanol spills will represent a much less severe hazard than gasoline, diesel fuel, or methanol spills.

- Methanol is more toxic than ethanol, but also disperses quickly in the environment. Its rapid dispersion will result in less severe environmental impacts than spills of petroleum-based fuels.

Detailed Information: Refer to page 10-4 through 10-5.

Issue #3: Land Contamination

Alcohol leaks and spills on land can poison terrestrial animal and plant life.

Implications of Land-Based Spills:

- Methanol, like gasoline and diesel, is very toxic to terrestrial plant and animal life but its effects are much shorter lived than those of petroleum-based fuels. Ethanol is not highly toxic and the effects of ethanol spills on land are not anticipated to be serious since ethanol dissipates quickly in the environment.

Proposed Solutions:

- Precautions in shipping and handling that are currently used for crude oil and gasoline will be sufficient for transporting methanol and ethanol.

Detailed Information: Refer to page 10-5.

Issue #4: Flammability and Leak Detection

Like gasoline and diesel, both ethanol and methanol are flammable liquids, and thus pose safety hazards. Moreover, leaks of methanol are difficult to detect, as is the fuel while burning.

- Methanol is odorless and lacks flame luminance under daylight conditions, making leaks difficult to detect and flames difficult to see.

- Due to higher points of ignition, both ethanol and methanol are much less flammable than gasoline or diesel. Thus, increased substitution of alcohols for gasoline/diesel will contribute to reducing the number of highway fires.

Proposed Solutions:

- The addition of additives such as nigrosine and gasoline would increase flame visibility.

- A distinctive agent to provide an odor to methanol needs to be identified and universally adopted, just as has been done for natural gas.

Detailed Information: Refer to page 10-5 through 10-6.

Section 10
HEALTH AND SAFETY ISSUES

- Toxicity
- Leaks and Spills in Water
- Leaks and Spills on Land
- Safety

Introduction

Modern society has become adept at producing, transporting, storing and dispensing a variety of transportation fuels. The key motor transportation fuels -- gasoline and diesel fuel -- have a number of serious drawbacks which require careful handling to prevent accidental poisoning and widespread ecological damage in the event of a transportation accident or leaking storage facility. Standard procedures have been developed to limit these risks to socially acceptable levels.

Concerns have been raised that the introduction of alcohol fuels (particularly methanol) into widespread use for transportation fuels will create new safety and health concerns. These concerns are of three types: toxicity; environmental damage in the event of a major water or land-based spill; and flammability.

Toxicity

A person may come into contact with a liquid motor fuel either through inhalation, ingestion, or dermal contact. Ingestion or swallowing is the most likely cause of serious acute poisoning. All of the existing motor liquid fuels, including ethanol, pose a toxic threat if sufficient amounts are ingested.

Diesel Fuel

Diesel fuel is highly toxic. [1] Its ingestion may cause nausea, vomiting, cramping, liver and kidney damage, lung irritation, and central nervous system depression ranging from a mild headache to coma, and death. Death would result from ingestion of just 63 ml (1/4 cup) for the average adult male. However, since diesel fuel will often cause regurgitation, large quantities of ingested fuel will often not stay in the stomach, thus avoiding the acute toxicity discussed above. Unfortunately, when regurgitation occurs, aspiration into the lungs of even small amounts of diesel fuel may result in severe irritation with coughing, gagging, difficulty breathing, chest pain, chemical pneumonitis and bronchopneumonia.

Gasoline

According to the American Association of Poison Control Centers (AAPCC), about 35,000 incidences of gasoline ingestion are reported annually in the United States. Most of them are a result of attempted siphoning from gasoline tanks. Gasoline is toxic if ingested in moderate quantities. Ingestion of even small amounts (5 to 10 ml) of gasoline may cause a burning sensation in the mouth, throat, and chest, and intense irritation and burning in the gastrointestinal tract with nausea, vomiting, diarrhea, and abdominal pain. Ingestion of 27 - 40 ml of gasoline will result in more serious symptoms including central nervous system depression, headache, dizziness, drowsiness, fever, and transient liver damage. Severe intoxication may cause unconsciousness and comma or convulsions with seizures. Fatal dose estimate for the average adult range from 115-180 ml to 470 ml, but death has been reported at a dose as low as 13 ml. The fatal dose for children is 13 to 20 ml. Gasoline is even more hazardous if aspirated into the lungs following regurgitation or belching. Once in the lungs, even small amounts may cause severe chemical pneumonitis, and death from lung insufficiency. Gasoline vapor is considered by the U.S. Environmental Protection Agency (EPA) to be a human carcinogen (with 68 incidences in 1986), and is suspected of causing various other chronic effects. [2] In addition, gasoline vapor contains benzene, a group of human carcinogens which was estimated to

cause 155 cancer incidences in 1986. [3] Gasoline's threshold limit value (TLV) of 300 ppm and short term exposure limit (STEL) of 500 ppm were set by EPA at least in part to protect against the cumulative toxic effects of benzene.

Methanol

Policy Issue #1

> Methanol is highly toxic. Ingestion of small quantities of methanol can cause blindness; large quantities cause death. Methanol poisoning can also occur by inhalation of the vapors or by prolonged exposure of the skin. Since methanol has no color, taste or odor, it has the potential to be ingested unintentionally more readily than the other liquid motor fuels.

The use of additives to provide a distinctive taste, color and odor to methanol would be beneficial. Various hydrocarbons in small amounts are successfully used as additives, such as in M85 (85% methanol, 15% gasoline).

Symptoms of overexposure to methanol result from methanol's metabolism in the body. Methanol is slowly metabolized to formate, which is in turn oxidized to form CO_2 which is then exhaled. Thus, in severe or long methanol exposure, the body's ability to metabolize the formate is overwhelmed, causing formate buildup and acidosis of the blood. The minimum lethal dose of methanol exposure in the absence of medical treatment generally ranges between 300 and 1000 mg/kg.

Ingestion is the most common form of methanol poisoning in humans. For the average adult male weighing 70 kg, toxic effects can begin with ingestion of as little as 18 ml (approximately 3 to 4 teaspoons), and as little as 26 to 70 ml can be fatal. However, there are cases described where as little as 6 ml proved fatal while in other cases 500 ml has not resulted in any permanent damage.

The normally fatal dose for methanol ingestion ranges from 60 to 240 ml. Since the toxic effects of methanol occur 10 to 48 hours after ingestion, there is sufficient time to seek medical attention. [4]

Ethanol

Ethanol is medically referred to as a hypnotic or depressant. It depresses activity in the upper brain and is also toxic if ingested in sufficiently large quantities, but it is much less toxic than methanol or gasoline. Generally, intoxication will bring sleep or unconsciousness before a toxic amount can be ingested. In rats, the lethal dose of ethanol is 13.7 g/kg of body weight [5] or 10-40 times greater than that for methanol. Abuse of ethanol is a major drug problem in most countries. U.S. federal law requires that some highly pure (generally 95-100%) ethanol used for scientific and industrial purposes be adulterated or "denatured" to discourage people from drinking it. Various denaturants are used, including methanol and gasoline.

Leaks and Spills in Water

Since methanol is infinitely soluble in water, a spill in open water disperses rapidly. In addition to its rapid dispersion, complete elimination from the environment occurs as a result of methanol's rapid biodegradation (decomposition of methanol as a result of natural processes). A wide variety of marine and terrestrial microbes metabolize methanol. [6] As a result, recolonization of methanol spill sites is very rapid (a matter of months) with no long-term effects, while the effects of petroleum spills may require years to disappear. Cleanup of methanol spills on water requires less effort and cost than petroleum fuel, and is generally more effective. For small spills, one only needs to monitor and isolate the area for several days, allowing natural biodegradation to complete the task. [7]

Policy Issue #2

In general, methanol is less toxic to marine life than petroleum fuels, and many of its poisoning effects are temporary and reversible.

Ethanol, like methanol, is biodegradable and infinitely soluble in water. Thus a spill in open water disperses rapidly. Ethanol is much less toxic than methanol and gasoline and its poisoning effects are handled much more easily.

Leaks and Spills on Land

Gasoline and diesel fuel are very toxic to terrestrial plant and animal life. [8,9] In this characteristic, it is similar to methanol. [10,11]

Policy Issue #3

Methanol, like the petroleum fuels, is very toxic to plant and animal life. However, the toxic effects of methanol spills are much shorter-lived than petroleum fuel spills, as discussed earlier.

Safety

Policy Issue #4

> The use of neat methanol and ethanol raises concerns about their lack of odor and lack of flame luminance. Concern over methanol (and to a lesser extent, ethanol) flame luminosity stems from the fact that methanol burns with a near invisible flame under daylight conditions.

An investigation into flame luminosity would consist of quantifying the flame luminance of methanol over the entire burn period. This would provide basic data to help in selecting a potential additive.

Nigrosine has been identified as a potential methanol luminosity enhancer. [12] The addition of 15 vol. % unleaded gasoline (M85) has also been suggested as a methanol fuel standard to increase flame visibility for safety reasons.

Because methanol, like natural gas, has no offensive odor which alerts users of a leak or spill, an agent must be introduced to provide a smell as an early warning. A fuel malodourant must be offensive enough to provoke instant recognition. Furthermore, the odor should be unique so that it will not be mistaken for other substances. **Butanethiol** has been identified as a promising malodourant, offering a relatively strong odor at a low concentration. [13]

Both the U.S. Department of Transportation and the National Fire Prevention Association (NFPA) classify methanol and ethanol as flammable liquids. Therefore, the federal codes and NFPA standards governing fire protection for transport, storage, and handling of flammable liquids are directly applicable to neat alcohol and blend fuels. [14]

Ethanol burns at a temperature of 13°C (55°F), and methanol at a temperature of 11°C (52°F). This is considerably higher than that of gasoline, which has a flame temperature of -43°C (-45°F).

Therefore, both ethanol and methanol are much less flammable than gasoline, and their use as liquid transportation fuels will contribute to reducing the number of fires caused by gasoline on U.S. highways every year.

ENDNOTES:

1. Litovitz, Toby, "Acute Exposure to Methanol in Fuels: A Prediction of Ingestion Incidence and Toxicity." National Capital Poison Center, October 31, 1988.

2. Adler, Jonathan M., and Penny M. Carey, "Air Toxics Emissions and Health Risks from Motor Vehicles." U.S. EPA, AWMA Paper No. 89-34A.6, July 1989.

3. Gabele, Peter A. et al, "Characterization of Emissions from Vehicles Using Methanol and Methanol-Gasoline Blended Fuels." FAPCA 35: 1168-1175, 1985.

4. Machiele, P. (1989). "A Perspective on the Flammability, Toxicity, and Environmental Safety Distinctions Between Methanol and Conventional Fuels", U.S. Environmental Protection Agency, Paper No. 43b, presented at the 1989 Summer National Meeting of the American Institute of Chemical Engineers, Philadelphia, PA, August 22, 1989.

5. Solomons, T.W.G., *Organic Chemistry*, 4th Ed., John Wiley & Sons, Inc. pp. 349-393, 1988.

6. Lawrence Livermore Laboratory, "Methanol as a Transportation Fuel: Assessment of Environmental and Health Research, December, 1980.

7. Argonne National Laboratory, "An Environmental Assessment of the Use of Alcohol Fuels in Highway Vehicles," December, 1980.

8. Environmental Protection Agency, "Cleanup of Releases of Petroleum USTS: Selective Technologies." EPA/530/UST-88/001, April 1988.

9. Letter to Charles R. Imbrecht, Chairman, California Energy Commission, from Dr. Peter D'Eliscu, Department of Biology, West Valley College, April 28, 1987.

10. D'Eliscu, Peter Neal. "Overview of Environmental Impacts from Methanol Fuel Spills." West Valley College, 1981.

11. D'Eliscu, Peter Neal. "Environmental Consequences of Methanol Spills and Methanol Fuel Emissions on Terrestrial